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13. ABSTRACT (Maximum 200 words) This annual technical report describes the continual superconductivity research on the materials and structural phases responsible for the above 200-K superconducting transitions, their synthesis conditions, and the study of the physical properties associated with these transitions. Superconducting resistive transitions and magnetic flux trapping phenomena have been observed in mixed-phase ceramic samples of YBaCuO (e.g. Y ₅ Ba ₆ Cu ₁₁ O _x) and on the surfaces of YBa ₂ Cu ₃ O ₇ single crystals in the temperature range 230 K to 270 K. Near room-temperature oxidation studies show that the properties can change, including a large resistance decrease over a 3-month period. This behavior is consistent with the formation of a different oxide phase on the surface of the grains. Structural analyses by x-ray diffraction and high-resolution transmission electron microscopy indicate these samples have surfaces with large amounts of defect structures as well. Correspondingly these surface phases/structures may be responsible for the above 200-K transitions.			
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Project Title: Investigations of YBaCuO Materials with Near-Room-Temperature Resistivity Transitions

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Technical Report for 1992 - 1993:

The main objectives of our superconductivity research are two-fold: (1) to understand the nature of the anomalous transitions with transition temperatures T_c above 200 K observed in some mixed-phase cuprate samples and (2) to improve the sample fabrication conditions so that samples showing the anomalies can be synthesized more consistently. To attain the first objective, measurements of the electrical resistivity, the current-voltage characteristics, the microwave effects, and the magnetization have been continually investigated on samples exhibiting anomalies above 200 K. To improve upon the fabrication conditions, the effects of the reaction temperature, cooling rate, and oxidation conditions have been studied. A brief summary of the progress made to date is briefly described below.

Electrical Measurements

As we have reported previously, the resistive transitions and current-voltage characteristics on several ceramic as well as single-crystal platelet samples of Y-Ba-Cu-O materials have exhibited superconducting-like transitions in the temperature range of 230 K to 270 K.[1-3] Other researchers[4] have made similar observations and provide some confirmation of our results.

Magnetic Measurements

Temperature-dependent magnetization measurements on several ceramic and single-crystal platelet samples of Y-Ba-Cu-O have shown hysteresis between the zero-field-cooled (ZFC) and the magnetic field-cooled (FC) curves with the onset of the hysteresis occurring above 200 K. This hysteretic behavior can be interpreted as superconducting flux trapping inside an inhomogeneous superconductor. ac susceptibility measurements on other ceramic samples have shown small diamagnetic signals equivalent to 1% or less of the diamagnetic signal resulting from the 90-K superconducting transition. C.Y. Huang has independently performed ac susceptibility measurements on some our samples and has observed a diamagnetic shift below 230 K.[5] More recently, we have observed transitions at 336 K on three different

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batches of Y-Ba-Cu-O samples. While the ZFC magnetization is featureless in the vicinity of 336 K, the FC magnetization shows a sudden increase below 336 K. Although this transition is detectable by the positive increase in the FC magnetization, this increase could be associated with a small Josephson screening current and the trapping of a large amount of magnetic flux. This type of "positive magnetization" in the FC magnetization data has been previously observed for BiSrCaCuO samples[6-8] as well as for a superconducting Nb disk.[9] Further characterizations are presently being pursued in order to elucidate the exact nature of this magnetic transition.

Microwave Measurements

In addition to the ac susceptibility measurements, Dr. Huang has also performed microwave experiments on the same sample which exhibited the diamagnetic shift at 230 K. A cavity resonance frequency shift has been observed at the same temperature of 230 K which is indicative of an inductance change associated with a superconducting transition.[5]

Material Synthesis and Characterization

The most successful route for synthesizing samples with T_c above 200 K has been by mixing an appropriate ratio of Y_2O_3 , $BaCO_3$, and CuO for a nominal sample composition of $Y_5Ba_6Cu_{11}O_x$ and multiple heatings to about 950°C with thorough grindings of the powder between heatings. The powder is subsequently cold-pressed into a pellet and annealed at 950°C followed by cutting the pellet into small pieces which are reannealed at 950°C in O_2 gas and rapidly cooled back to room temperature. X-ray diffraction patterns show that these pieces are multi-phase with $YBa_2Cu_3O_{7-\delta}$ and Y_2BaCuO_5 being the predominate structures. High-resolution transmission electron microscopy studies revealed numerous defect structures in the CuO_2 planes. Energy dispersive x-ray spectroscopy indicate a deficiency of Cu near the surface, yielding roughly $YBa_2Cu_{2.7\pm0.2}O_x$. It should be noted that the Zürich group[10] has reported observing diamagnetism at 120 K in $YBa_2Cu_{2.78}O_7$ single crystal samples. This suggests that defects in Y-Ba-Cu-O materials may play an important role in enhancing T_c .

Oxidation Studies

One critical condition for observing and reproducing a zero-resistance transition having a T_c above 200 K is to keep the sample in an O_2 environment continuously during the measurements and thermal cyclings. This effect has been confirmed by a group at the University of Regensburg.[4] However in other experiments, such as microwave and magnetization measurements, the anomalous high- T_c phenomena can be observed even when the samples are not kept in oxygen environment. One possible explanation for these different experimental observation conditions is that the diffusion of oxygen molecules into a solid at

low temperatures is limited. Thus this results in only the material near the surface of grains being affected by diffusion of oxygen and the formation of granular shells of the higher T_c material. In microwave and magnetization measurements, disconnected granular shells can still contribute to an observable signal even though flux trapping will dominate the magnetization response. However, the observations of zero-resistance and bulk-like Meissner effect require a continuous intergranular path of these "good" surfaces, i.e., good connectivity between granular shells of the higher- T_c material. In order to determine the effect of low-temperature oxygen diffusion (equivalent to near room-temperature annealing) on the Y-Ba-Cu-O materials, the resistivity of one sample has been monitored over a three-month period which has been continuously kept in O_2 gas at 2 atm and at 350 K or below. Not only did the resistance decrease by an order of magnitude at room temperature during this time, but the temperature dependence changed from a linear to a concave upwards behavior, a clear indication of a material change caused by low-temperature oxidation. Furthermore the decrease in the resistance over time can be understood in terms of the growth of the shell thickness covering the grain. Using a simple model calculation involving three geometric parameters (the radius of the grain, the shell thickness, and the intergranular contact depth) and an exponential diffusion of oxygen with time (i.e., the growth of the shell having zero resistance), the calculated results agree qualitatively with the experimental data. This further supports our speculation that a different oxide phase on the surfaces of grains can be formed near room temperature and may be the phase responsible for the anomalously high- T_c superconductivity.

Future Objectives

During the next year, our plans are to continue the near-room-temperature oxidation studies and to expand the studies to include higher O_2 pressures, electrochemical oxidation, and ozone treatments in order to determine the effect upon the material properties above 200 K and ultimately to find better synthesis conditions for reproducing samples which exhibit higher superconducting transition temperatures. In addition to our electrical and magnetic measurements, we will continue to utilize DTA/TG measurements, x-ray diffraction studies, and optical and electron microscopy studies to assist in the material characterizations.

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Papers and Abstracts:

L-Q. Wang, M.S.M. Minhaj, J.T. Chen, and L.E. Wenger, "Construction of a simple low-field solenoid for the Quantum Design® SQUID magnetometer", Rev. Sci. Instrum., accepted.

M.S.M. Minhaj, S. Meepagala, J.T. Chen, and L.E. Wenger, "Thickness dependence on the superconducting properties of thin Nb films", Phys. Rev. B, submitted.

Talks:

J.T. Chen, L.E. Wenger, L-Q. Wang, C.H. Chen, and D.J. Werder, "Measurements, Processings, and Structures of Y-Ba-Cu-O Materials with Anomalous Transitions near 260 K", invited talk, Symposium on Processing and Applications of High T_c Superconductors, Ben Franklin Superconductivity Center, Philadelphia, PA, 29 June 1992.

L.E. Wenger, "Search for Room-Temperature Superconductivity", seminar, Miami University, OH, 7 October 1992.

L.E. Wenger and J.T. Chen, "Experimental Evidence for Superconductivity above 200 K", Near-Room-Temperature Workshop, Bodega Bay, CA, 19 October 1992.

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